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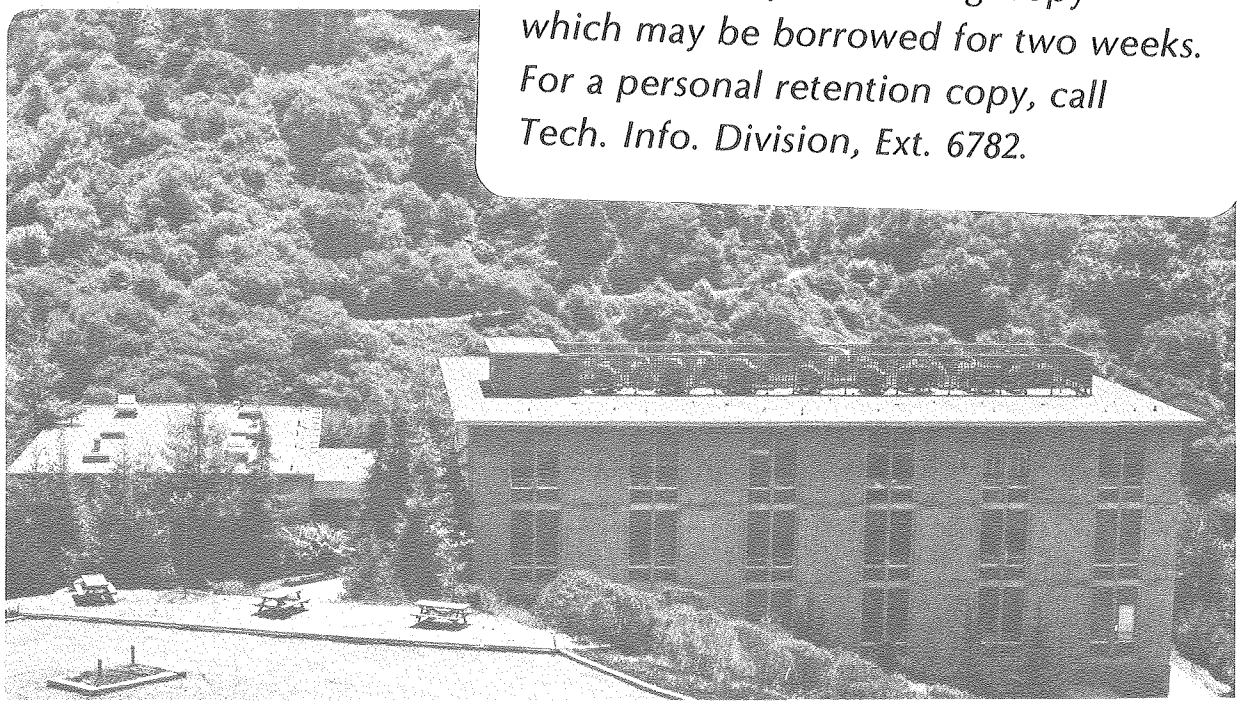

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ANHARMONICITY, PHONON LOCALIZATION, TWO-PHONON BOUND STATES AND VIBRATIONAL SPECTRA

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Abstract

Neither local modes nor extended phonons precisely describe the excitations of anharmonic solids. A simple model Hamiltonian presented here characterizes the transition from local oscillator to optical phonon which would take place if one could continously increase the phonon dispersion. The model is used to describe two types of transitions: a phonon localization transition which is the analogue of the Mott transition for electrons, and a spectral transition associated with the appearance of two-phonon bound states. In real materials, a sharp phonon localization transition is probably not achievable, but striking spectral effects may be observable for some systems which are marginally able to produce two-phonon bound states.

I. Introduction

The harmonic approximation is usually taken as a fundamental tenant of solid state physics. Noninteracting phonons are a consequence of the harmonic approximation, and small deviations from harmonicity can be treated perturbatively in terms of phonon-phonon interactions.

The limitations of the harmonic approximation are much more apparent in molecular physics than they are in solid state physics. Small variations in the spacing between molecular vibrational energy levels result from anharmonicity, and although the deviations from harmonicity may be small, they have important consequences. For example, molecular vibration spectra change with the vibrational excitation of the molecules, and absorption peaks can exhibit saturation and power broadening.[1,2] These phenomena are not commonly encountered in solids where the absorption peaks correspond to small-wave-vector-phonon energies even when a large number of phonons have been excited.

The apparent success of the harmonic approximation in solids results from phonon dispersion. If one views a solid as a collection of molecular units, dispersion of the optical phonons results from intermolecular coupling. When this coupling dominates the anharmonicity, deviations from harmonicity become difficult to observe.

The goal of this paper is to describe the hypothetical transition from a collection of anharmonic oscillators to a set of interacting phonons which would occur if one could continuously increase the phonon dispersion from zero until it dominates the anharmonicity. Our basic conclusion is that one should really think of two different

transitions; a "phonon localization transition" which is analogous to the Mott transition for electrons[3], and a "spectral transition" associated with a change in the character of the infrared absorption.

The first transition, phonon localization, is a cooperative effect, and because of this it is predicted to occur only when the optical phonon density is appreciable. In practice, one may only be able to produce a sufficient phonon density to observe this transition in microscopic systems. We see little prospect of finding real macroscopic systems for which phonon localization would be anything like a true phase transition.

The spectral transition is never a phase transition. Rather, it is a change in the character of the elementary excitations which occurs as the physical parameters of the system ($\sim$ dispersion/anharmonicity) are changed. This transition is closely related to the possibility of forming two-phonon bound states. We associate phonons with a linear combination of single vibrational excitations on each molecule, and two-phonon bound states with double vibrational excitations of single molecules. Typical "molecular" phenomena, such as saturation, can occur only if the phonon dispersion is small enough compared with the anharmonicity to permit the formation of these bound states. The spectral transition coincides with the appearance of the bound states. Phonon dispersion which is near the critical transition value will lead to anomalous spectral features.

Our investigation of anharmonic phonon systems is based on a simple model Hamiltonian which is developed in the following section and in Appendix A. The model is constructed so that the ratio of dispersion to anharmonicity is a free parameter. By varying this

parameter, we are able to describe the phonon localization transition (Section III), the appearance of two-phonon bound states (Section IV and Appendix B), and the spectral transition (Section V).

II. Model Hamiltonian

A simplified model of a system of coupled local anharmonic oscillators is presented here. One can think of each oscillator as corresponding to a given vibrational mode of a single molecule in a molecular crystal. Alternatively, the oscillators may correspond to the set of degenerate stretching modes in a single molecule--like the C-H bonds in benzene. The most important simplification (and limitation) of this model is that it considers only one optical mode or phonon branch, and the coupling to other optical modes and acoustic phonons is ignored. One consequence of this is that the mode or phonon decay processes are neglected.[4,5,6]

The only important anharmonicity in the model is assumed to be "intramolecular", so the potential energy need only be expanded to second order in the "intermolecular" coupling, but intramolecular terms up to fourth order are included in the Hamiltonian. If x_n and p_n are the relevant normal coordinate and conjugate momentum of the n^{th} oscillator, then the classical Hamiltonian is

$$H_C = \sum_n \left(\frac{p_n^2}{2m} + \frac{1}{2} K x_n^2 + \gamma_3 x_n^3 - \gamma x_n^4\right) + \sum_{n<m} D_{nm} x_n x_m \,, \qquad (1)$$

where m is the effective mass and K is the spring constant of the oscillator, γ_3 and γ are anharmonic coefficients, and the D_{nm} are the coefficients of intermolecular coupling. We assume that anharmonic and intermolecular effects are relatively small. This assumption means

$$\sum_m |D_{nm}| \ll K,$$

$$|\gamma_3 \bar{x}| \ll K \quad , \tag{2}$$

$$|\gamma \bar{x}^2| \ll K \quad ,$$

where $\bar{x}$ is a root-mean-square value of any of the x_n.

To lowest order, the classical Hamiltonian describes a set of harmonic oscillators, so it is natural to quantize the Hamiltonian through the substitution

$$\begin{aligned} x_n &\rightarrow \sqrt{\frac{\hbar}{2\sqrt{Km}}}\,(a_n^+ + a_n) \quad , \\ p_n &\rightarrow \sqrt{\frac{\hbar\sqrt{Km}}{2}}\, i(a_n^+ - a_n) \quad . \end{aligned} \tag{3}$$

Here a_n^+ (a_n) corresponds to a "local" phonon creation (annihilation) operator. When x_n and p_n are replaced by the appropriate creation and annihilation operators, the resulting Hamiltonian has both "phonon-conserving" and "phonon-nonconserving" terms. The phonon-conserving part of the Hamiltonian, H, is essentially a Bose version of the Hubbard model[7] with attractive interactions.

$$H = \sum_n \varepsilon\, a_n^+ a_n + \sum_{nm} \Delta_{nm} a_n^+ a_m - \Gamma \sum_n a_n^+ a_n^+ a_n a_n \tag{4}$$

The zero-order phonon energy, ε, "hopping" matrix elements, Δ_{nm}, and phonon-phonon interaction strength, Γ, are determined from the corresponding coefficients appearing in the classical Hamiltonian, H_c in Eq. (1). We will take the phonon conserving Hamiltonian of Eq. (4) as our basic model. In Appendix A it is shown that the terms left out of this Hamiltonian are unimportant since they can be largely eliminated through a similarity transformation if the conditions of Eq. (2) are met. The similarity transformation renormalizes the energies ε, Δ_{nm}, and Γ.

The model Hamiltonian of Eq. (4) must be approached with caution. Formally, it is not well defined if Γ is positive since it then describes a system of Bosons with attractive interactions, and the energy of the system can become arbitrarily negative.[8] This difficulty can be circumvented when necessary by an appropriate restriction of the allowed states of the system.

In many ways, the physics of systems described by the model Hamiltonian (Eq. (4)) depends on only one parameter; the relative size of Γ compared to Δ_{nm}. If the Δ_{nm} are zero, the model reduces to a set of anharmonic oscillators with energy levels.

$$E_\ell = \ell\varepsilon - \Gamma\ell(\ell-1) \tag{5}$$

On the other hand, if Γ is zero the Hamiltonian can be diagonalized. For example, if N oscillators are distributed along a line with periodic boundary conditions, and Δ is nonzero only for nearest-neighbor interactions, then the Hamiltonian can be written as

$$H = \sum_q \left[\varepsilon + \frac{W}{2}\,\mathrm{sgn}(\Delta)\,\cos(q)\right] a_q^+ a_q \tag{6}$$

where $W = 4\Delta$ is the phonon bandwidth, $\mathrm{sgn}(\Delta)$ is the sign of Δ, and

$$a_q^+ = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{-iqn}\, a_n^+ \tag{7}$$

is the creation operator for a delocalized phonon with crystal momentum $\hbar q$. Note that zone-center phonon energy is shifted away from the "molecular" energy, ε, by $\frac{1}{2}W\mathrm{sgn}(\Delta)$. The sign of Δ ($\mathrm{sgn}(\Delta)$) will turn out to have a significant influence on the behavior of the spectral transition discussed in Section V.

For many materials, the important parameters Γ and W which characterize this model can be approximated. Intramolecular anharmonicity Γ can be obtained from molecular spectra.[9] Herzberg[10] has tabulated

values of Γ (called $\omega_e x_e$ in his Table 39) for a great many diatomic molecules in units of cm^{-1} (= 1.23×10^{-4} eV = 1.44 K_B degree).[11] Three examples are

$$\Gamma = 117.9\ cm^{-1} \quad \text{for } H_2 \tag{8}$$
$$\Gamma = 52.05\ cm^{-1} \quad \text{for HCl}$$
$$\Gamma = 11.67\ cm^{-1} \quad \text{for } C_2$$

The second important quantity is the phonon bandwidth, W, which is determined from the values of Δ_{nm}. Estimates of W come from theoretical calculations and experimental evidence such as neutron scattering and Davydov splitting. Optical phonon bandwidths for the solid forms of the materials sited above are

$$W \cong 4\ cm^{-1} \text{ for solid molecular parahydrogen}[12]$$
$$W \cong 50\ cm^{-1} \text{ for solid HCl}[13] \tag{9}$$
$$W \cong 130\ cm^{-1} \text{ for diamond}[14]$$

The width W in HCl is considerably larger than it is in H_2 because long range electrostatic interactions are small in hydrogen.[13]

In our model, the really significant measure of anharmonicity is the ratio W/Γ,

$$W/\Gamma \cong 1/30 \text{ for hydrogen}$$
$$W/\Gamma \cong 1 \text{ for HCl} \tag{10}$$
$$W/\Gamma \cong 11 \text{ for diamond}$$

The parameters Γ and W obtained for these three examples are typical. Thus we feel that most ordinary semiconductors, like diamond, are too weakly anharmonic to exhibit striking phonon localization effects like two-phonon bound states. Some molecular solids like H_2 which exhibit very little phonon dispersion will clearly show molecular properties. The most interesting cases will be molecular solids like HCl in which the phonon dispersion and anharmonic effects are equally important.

There are other materials where this model Hamiltonian might profitably be applied because dispersion and anharmonicity are comparable. The transition-metal carbides[15] and metal hydrides and deuterides[16] are interesting possibilities. For example, the optical mode frequencies in NbC form a fairly narrow band ($W \lesssim 80\ cm^{-1}$) and one optical phonon cannot decay into two acoustic phonons and conserve energy. Optical phonon bandwidths seem to vary a great deal in metal hydrides and deuterides. In $PdD_{0.63}$, $W \lesssim 100\ cm^{-1}$, but in $NbD_{0.75}$, W is probably less than $20\ cm^{-1}$.[16] The anharmonicity parameter, Γ, in these materials may be quite large because of hydrogen's small mass.

III. Phonon Localization Transition

In general, exact eigenstates of the model Hamiltonian developed in the previous section will be extremely complex.[8] We would like to know whether the basic physics of this model is better described in terms of phonons or local oscillators. Here, we base our criterion for selecting between these two limits on estimates of the free energy The true free energy of the system is, of course, independent of the way we describe the system, but the approximate free energy estimated from the perturbation approach does depend on which part of the Hamiltonian is chosen as the unperturbed Hamiltonian. Extended phonons are assumed to be "stable" only if they yield a lower approximate free energy than the local oscillators.

The Hamiltonian of our system can be separated into two parts

$$H = H_o + \delta H \tag{11}$$

with H_o and δH being the unperturbed Hamiltonian and the perturbation

respectively. Then, the true free energy of the system has an upper bound.[17]

$$F \leq F_0 + \langle \delta H \rangle_0 , \tag{12}$$

where F_0 is the free energy of a system described by H_0, and $\langle \delta H \rangle_0$ denotes the thermodynamic average of δH in the H_0 system.

The two obvious choices for H_0 correspond to treating either the phonon hopping or the anharmonicity as a perturbation. In the former case corresponding to the local oscillator description, we take the "local" part of H as H_0.

$$H_{loc} = \sum_n (\varepsilon\, a_n^+ a_n - \Gamma\, a_n^+ a_n^+ a_n a_n) , \tag{13}$$

so

$$\delta H = \sum_{n \neq m} \Delta_{nm}\, a_n^+ a_m . \tag{14}$$

In this case, it is found that $\langle \delta H \rangle_0 = 0$, and

$$F_{loc}/N = -\frac{1}{\beta} \mathrm{Ln}(Z) . \tag{15}$$

Here (see Eq. (5))

$$Z = \sum_{\ell=0}^{\infty} \exp(-\beta[\ell\varepsilon - \ell(\ell - 1)\Gamma]) , \tag{16}$$

and β is the inverse temperature in units of Boltzmann's constant. Formally, Z does not exist (for positive Γ) because its power series diverges. However, we restrict ourselves to the case where the average excitation of each local oscillator is so limited that for all levels that are significantly populated, $\beta\ell(\ell\text{-}1)\Gamma \ll 1$. Then the system has an approximate partition function

$$Z' = \sum_{\ell=o}^{\infty} [1 + \ell(\ell\text{-}1)\beta\Gamma + \tfrac{1}{2}\ell^2(\ell\text{-}1)^2\, \beta^2\Gamma^2 + \ldots.] \exp(-\beta\ell\varepsilon) .$$

To order $(\beta\Gamma)^2$ the local free energy obtained from Z' is

$$\frac{F_{loc}}{N} = \frac{1}{\beta} \mathrm{Ln}\,(1\text{-}e^{-\beta\varepsilon}) - 2\Gamma n^2 - 2\beta\Gamma^2 n^2 (n+1)(5n+1) , \tag{17}$$

where the Bose factor

$$n = (e^{\beta\varepsilon} - 1)^{-1} \tag{18}$$

gives the average number of phonons per oscillator assuming Γ and Δ are zero.

For the case corresponding to the phonon description, the anharmonicity is written as a phonon-phonon interaction and is treated perturbatively. We take H_o to be a mean-field approximation of H, that includes not only the harmonic part of H but also the mean field contribution from the anharmonic terms in H. Then, δH contains only corrections to the mean field approximation from the anharmonic terms. This case is more clearly described if we make the model a little more specific. So we assume a simple lattice of oscillators. The index n labels an oscillator at a lattice point $\vec{R}_n$, and the phonon hopping parameters Δ_{nm} depend only on the relative separation $(\vec{R}_n - \vec{R}_m)$. If Γ were zero, the Hamiltonian on the lattice could be written simply in terms of extended phonon operators. (A simpler one-dimensional case is given in Eqs. (6) and (7)).

$$H(\Gamma = 0) = \sum_q \varepsilon_q \, a_q^+ \, a_q, \tag{19}$$

where

$$\varepsilon_q = \varepsilon + \sum_n e^{iq(R_n - R_m)} \Delta_{nm} \tag{20}$$

and

$$a_q^+ = \frac{1}{\sqrt{N}} \sum_n e^{-iq\cdot R_n} \, a_n^+ \quad . \tag{21}$$

The sum over q is restricted to the Brillouin zone, and N is the number of lattice points. For $\Gamma \neq 0$, the anharmonic terms can also be written in terms of the extended phonon operators.

$$-\Gamma \sum_n a_n^+ a_n^+ a_n a_n = -\frac{\Gamma}{N} \sum_{k_1, k_2, q} a_{k_1+q}^+ \, a_{k_2-q}^+ \, a_{k_2} \, a_{k_1} \tag{22}$$

If one requires that H_o be a single-particle Hamiltonian, minimization of the free energy is equivalent to making a Hartree-Fock-like factorization of the interaction term in the Hamiltonian. That is, if (1,2,3,4) correspond to specific k-vectors,

$$a_1^+ a_2^+ a_3 a_4 \rightarrow \left\{ \begin{array}{l} \langle a_1^+ a_4 \rangle_o \; a_2^+ a_3 + \langle a_2^+ a_3 \rangle_o \; a_1^+ a_4 \\ + \langle a_1^+ a_3 \rangle_o \; a_2^+ a_4 + \langle a_2^+ a_4 \rangle_o \; a_1^+ a_3 \end{array} \right\} . \tag{23}$$

The only nonzero thermodynamic averages are $\langle a_k^+ a_k \rangle_o$. This means that in the zeroth order, the interaction term in the Hamiltonian gives a mean field contribution with

$$-\Gamma \sum_n a_n^+ a_n^+ a_n a_n \rightarrow \; - 4 \frac{\Gamma}{N} \sum_k \langle a_k^+ a_k \rangle \sum_q a_q^+ a_q \; . \tag{24}$$

Let C be the number of optical phonons per oscillator

$$C = \frac{1}{N} \sum_K \langle a_K^+ a_K \rangle$$

Then the unperturbed Hamiltonian H_o in this case becomes

$$H_{MF} = \sum_q (\varepsilon_q - 4 C\Gamma) \; a_q^+ a_q \; . \tag{26}$$

The energy shift of each phonon ($-4C\Gamma$) is twice what a naive guess would suggest. The free energy is obtained from Eq. (12). Since we have assumed that $\beta\Gamma << 1$ and $\beta\Delta << 1$, we keep terms only up to order $(\beta\Gamma)^2$ and $(\beta\Delta)^2$. We find

$$\frac{F_{MF}}{N} = \frac{F_{loc}}{N} - \beta \bar{W}^2 \; n(n+1)/2 + 2\beta\Gamma^2 \; (n(n+1))^2 \; , \tag{27}$$

where n is still the phonon occupation number given by Eq. (18), and

$$\bar{W} = \sqrt{\sum_m \Delta_{nm}^2} \tag{28}$$

is comparable to, but somewhat smaller than the bandwidth parameter tabulated in Eq. (9). Typically, $\bar{W} \simeq W/3$. Since n increases with temperature, F_{MF} becomes larger than F_{loc} at a sufficiently high

temperature, and the localized oscillator becomes "stable". In other words, the localized oscillator description is more appropriate. The approximate phase boundary between localized oscillators and delocalized phonons is obtained by letting $F_{loc} = F_{MF}$, and the result is

$$\sinh(\varepsilon/(K_B T^*)) = \Gamma/\bar{W} , \tag{29}$$

where T^* is the transition temperature. This equation was used to construct the phase diagram shown in Figure 1. As can be seen in this figure, the hypothetical transition from anharmonic oscillators to interacting phonons occurs in our model as $\bar{W}/\Gamma$ increases from zero to a large number. Since the phonon density is related to the temperature, a transition from localized to extended phonons also occurs if the temperature is decreased and the ratio $\bar{W}/\Gamma$ is held constant. This behavior is in contrast to the metal-insulator transition where increasing temperature generally delocalizes electron states.[3]

The above phonon localization transition corresponds to a gradual change in the nature of the vibrational excitations of the system and is not a true phase transition. For $\bar{W} \gtrsim \Gamma$, the transition appears at $K_B T^* \gtrsim \varepsilon$. A temperature high enough to excite a significant number of phonons ($K_B T \approx \varepsilon$) would be much higher than the temperature that characterizes the interaction energy of particles ($K_B T_C \approx \bar{W}$ or Γ); the phonons become a hot fluid. For very small $\bar{W}/\Gamma$, Figure 1 predicts a low transition temperature, but the mean-field approximations used here are inaccurate for the case of a dilute gas of strongly interacting phonons.[18]

There is a practical reason why the phonon localization transition described here may be difficult to observe. It is simply not easy to put a large number of phonons into a phonon band. Optical phonon

lifetimes are generally not long (10^{-11} sec is a typical number). This means that one probably cannot excite a sufficiently large number of phonons in a given optical band through optical pumping to observe the phonon localization transition. Thermal excitation of a large number of optical phonons is not likely in molecular solids because these materials have relatively low melting or dissociation temperatures, T_M, and $K_B T_M \ll \varepsilon$. A large number of optical phonons can be thermally produced in semiconductors like diamond for a high T_M. For such materials, however, $\Gamma/\bar{W}$ is small, and hence T^* is still greater than T_M. For example, $K_B T_M \sim 2\varepsilon$ and $\bar{W}/\Gamma \cong 3.5$ for diamond, so that $K_B T^* \cong 3\varepsilon$ and $T^* > T_M$. (Also, the diamond-to-graphite transition becomes increasingly likely as the temperature is raised.) It is possible that a gradual phonon localization could be observed in some other material where $K_B T_M > \varepsilon$, but we have not yet been able to find a reasonable candidate.

Even though a true phonon localization phase transition is probably difficult to observe in macroscopic systems such as solids, one can find small systems in which localization effects have been observed. The benzene molecule is a good example.[19-23] The highest frequency modes in benzene correspond to stretching of the C-H bonds. The model Hamiltonian can be applied to this molecule if it is viewed simply as a set of six coupled vibrational units with $\Gamma = 57.6$ cm^{-1}[17] and $W \cong 35$ cm^{-1}.[19] It is possible to highly excite the C-H bonds for example, from $\nu = 0$ to $\nu = 1$-9. The measured excitation energies of singly or doubly excited benzene correspond to phonon frequencies if phonons are interpreted as vibrational modes of the entire molecule. However, the energies of the higher excitations ($\nu = 5$ to 9) correspond more close-

ly to the energies of an isolated anharmonic C-H bond. Thus the vibrations in benzene appear to undergo a transition from extended to localized modes as the energy (or effective temperature) of the system is increased. Physically, phonon localization is associated with small transport coefficients. This means that it will take a relatively long time for the energy to diffuse away from a single highly excited C-H bond in benzene.

Phonon localization transistions can probably also appear in molecular doped crystals, such as pentacene in benzoic acid. Higher doping concentration decreases the distance between impurity molecules, increases the intermolecular coupling, and may induce a dispersion in their coupled molecular vibration. Yet the impurity system may still be small enough, and the corresponding phonon lifetime may be long enough, so that a phonon localization transition could occur.

IV. Two Phonon Bound States

Excitations which we would now call two-phonon bound states have been known for a long time. For example, Gush, et al., observed "double transitions" in solid hydrogen in 1957.[24] More recently, Cohen and Ruvalds interpreted an anomaly in the two-phonon Raman spectrum of diamond in terms of two-phonon bound states.[25] This interpretation stimulated a good deal of interest and criticism.[26-29]

Two-phonon bound states are of obvious interest because they can be observed spectroscopically.[9] In addition, we believe that these bound states are closely related to the spectral transition, to be discussed in Section V. There we will argue that systems which can support bound states are sufficiently "molecular" to show effects

normally associated with the absorption spectrum of isolated molecules.

Here, we consider bound states of the model Hamiltonian for a one-dimensional lattice, and an artificial three-dimensional system characterized by a semicircular density-of-states. Much more elaborate two-phonon bound state calculations have been performed by Bogani and others.[9,13,29-31] Our presentation here may still be of interest because of its relative simplicity.

We first consider two phonons in the one-dimensional lattice described by Eqs. (6) and (7). For this case, any two phonon wavefunction can be written as

$$|\psi\rangle = \frac{1}{\sqrt{2N}} \sum_{n,m=1}^{N} g_{nm}\, a_n^+ a_m^+ |0\rangle \,, \tag{30}$$

with $g_{nm} = g_{mn}$. Since the system is translationally invariant, one should consider only those $|\psi\rangle$ which are also eigenstates of the translation operator, and then,

$$g_{nm} = \exp(iq(n+m)/2)\, g(n-m) \tag{31}$$

where q is the center-of-mass wavevector of the system, and $|q| \leq \pi$. We introduce new basis states $|m_q\rangle$ which simplify the notation.

$$|m_q\rangle = \frac{1}{\sqrt{2N}} \sum_{n=1}^{N} e^{iq(n+m)/2}\, a_n^+ a_{n+m}^+ |0\rangle \tag{32}$$

Physically, $|m_q\rangle$ describes two phonon excitations separated by m sites with a total crystal momentum $\hbar q$. Any two phonon wavefunction with a wavevector q can be written as a linear combination of the $|m_q\rangle$. For example, the state $|\psi_F\rangle$ which describes two free phonons with wavevectors k_1 and k_2 is

$$|\psi_F\rangle = \sqrt{\frac{2}{N}} \sum_{m=1}^{N} \cos((k_1 - k_2)m)|m_q\rangle \,, \tag{33}$$

if $q = k_1 + k_2$.

We are interested in finding the bound state energy and wave function. This is carried out in Appendix B. In the derivation, we need to evaluate $\langle m'_q| H|m_q\rangle$. The model Hamiltonian of Eq. (4) appears to have a simple form when its actions on the states $|m_q\rangle$ is considered.

$$H|m_q\rangle = 2\varepsilon|m_q\rangle + 2\Delta \cos(q/2)(|[m+1]_q\rangle + |[m-1]_q\rangle) - 2\Gamma\delta_{mo}|0_q\rangle \qquad (34)$$

The above equation shows how the physics of two interacting phonons is closely related to the physics of a single particle with "hopping" matrix element $2\Delta\cos(q/2)$ subjected to a static "impurity potential" of strength -2Γ at the origin. The two-phonon system can be regarded as equivalent to a single-particle system. The symmetry of the two phonon wavefunction means that the only physically significant states of the equivalent single particle system are symmetric with respect to $|m_q\rangle \rightarrow |-m_q\rangle$. Two-phonon bound states are equivalent to single particle states which are bound to the "impurity". The bound state energy for the above one-dimensional system is found to be (see Appendix B)

$$E_B = -2\sqrt{\Gamma^2 + (2\Delta \cos(q/2))^2} + 2\varepsilon \ , \qquad (35)$$

For large Γ, E_B approaches the energy of the doubly excited anharmonic oscillator, and for small Γ, E_B approaches twice the minimum phonon energy. The bound state wavefunction obtained from $H|\psi_B\rangle = E_B|\psi_B\rangle$, is

$$|\psi_B\rangle = \sqrt{\frac{1+r^2}{1-r^2}} \sum_{m=-N/2}^{N/2} r^{|m|} |m_q\rangle \ , \qquad (36)$$

where

$$r = -\mathrm{sgn}(\Delta)\ (\sqrt{\Gamma^2 + (2\Delta \cos(q/2))^2} - \Gamma)/(2\Delta \cos(q/2)) \ , \qquad (37)$$

The overlap of the two phonon bound state $|\psi_B\rangle$ with the wavefunction describing two free phonons $|\psi_F\rangle$ is of particular interest. As we shall see later in Sec V, the square of this matrix element, $|\langle\psi_B|\psi_F\rangle|^2$, is proportional to the oscillator strength of exciting a two-phonon bound state from a single-phonon state. Assuming that k_1 and k_2 which determine $|\psi_F\rangle$ are small, but not identical, we let

$$R = \frac{N}{2}|\langle\psi_F|\psi_B\rangle|^2 = (\Gamma^3)\{(\sqrt{\Gamma^2 + (2\Delta)^2} + 2\Delta)^2 \sqrt{\Gamma^2 + (2\Delta)^2}\}^{-1} \quad (38)$$

The factor N/2 is chosen to normalize R to unity for large Γ. Clearly R can be considerably enhanced or suppressed depending on the magnitude of Γ and the sign of Δ.

Except for some quasi-one-dimensional systems like polymers,[32] it is somewhat unrealistic to consider bound states of the one-dimensional model, since any nonzero Γ can lead to bound states. Three-dimensional bound states appear only for Γ greater than some minimum value. Exact calculations of the properties of three-dimensional bound states in a lattice require numerical work, so for clarity we consider a ficticious system called the "semicircular model"[7] in which the single-phonon energy levels form a semicircular density of states, $\rho(E)$, of width W.

$$\rho(E) = \frac{2}{\pi W^2}\sqrt{W^2 - (2(E-\varepsilon))^2} \quad (39)$$

We consider only the two-phonon bound state with center-of-mass wavevector equal to zero, and assume that a single q = 0 phonon has an energy $\varepsilon_0 = \varepsilon \pm W/2$ with the sign of W/2 determined by the sign of Δ.

Making these assumptions, one can establish the properties of the bound states using the Greens function methods commonly employed for static impurity problems[33] (see Appendix B). We find that a q = 0

bound state can be formed only if $W < 4\Gamma$, and the bound state energy is

$$E_B = 2\varepsilon - \frac{W}{2}\left(\frac{4\Gamma}{W} + \frac{W}{4\Gamma}\right) \quad . \tag{40}$$

The two-phonon continuum (two free phonons) and bound state energy levels as a function of W/Γ (for the semicircular model) are shown in Figure 2. The normalized probability, R, for forming bound states out of $|\psi_F\rangle$ for the semicircular model is also obtained in Appendix B.

$$R = (4\Gamma)^2 (4\Gamma - W\cdot\mathrm{sgn}(\Delta))/(4\Gamma + W\cdot\mathrm{sgn}(\Delta))^3 \tag{41}$$

When W is close to 4Γ, R can either be considerably greater than or less than 1 depending on the sign of Δ. Values of R as a function of W/Γ for the semicircular model are shown in Figure 3. The upper curve corresponds to negative Δ and the lower curve corresponds to positive Δ. Note the logarithmic scale for R in this figure.

V. Infrared Absorption and the Spectral Transition

Measurements of the infrared absorption spectrum provide an important probe of phonon systems. We will investigate the infrared absorption of the model Hamiltonian of Section II, and show that this absorption depends sensitively on W/Γ. The model exhibits a transition from a phonon-like to a molecule-like system as W/Γ is decreased to the point where two-phonon bound states can appear ($W/\Gamma = 4$ for the semicircular model). We will also show that when W/Γ approaches this critical value from below, saturation effects can either be considerably enhanced or suppressed depending on the sign of Δ.

As a first step we calculate the linear response of the model Hamiltonian to an applied radiation field. The perturbation of the

Hamiltonian is taken to be

$$H' = -e^* \sum_n x_n E(n,t) . \tag{42}$$

Here, e^* is the effective oscillator charge, E(n,t) is the electric field directed along x_n at the n^{th} oscillator site at time t. The coordinate x_n can be written as $(a_n^+ + a_n)(\hbar/(2\sqrt{Km}))^{\frac{1}{2}}$ using Eq. (3). Strictly speaking, H' should be subjected to the similarity transformation described in Section II and Appendix A. Among other things, this transformation would incorporate many-phonon processes into the linear response function.[9] However, the similarity transformation yields a small correction to the overall absorption and it will be ignored here. The linear response approach taken here also neglects polariton effects.[34]

The power absorbed by the model system is

$$P = \frac{e^*}{m} <\sum_n p_n E(n,t)>, \tag{43}$$

where the oscillator momentum is $p_n = (a_n^+ - a_n)\, i\, (\hbar\sqrt{Km}/2)^{\frac{1}{2}}$ and <> is a time average. The linear response is obtained by calculating $<P>/E^2$ to first order in H'. Assuming the system is initially in an eigenstate $|j>$ of the unperturbed Hamiltonian, and the electric field is characterized by a wavevector q and a positive frequency ω, the normalized absorption coefficient is

$$\alpha(\omega)_j = \sum_m \{ |<m|\, a_q^+ |j>|^2 - |<m|a_q|j>|^2 \}\, \delta(\omega - |\omega_m - \omega_j|) , \tag{44}$$

with $\int_0^\infty \alpha(\omega)d\omega = 1$. Here a_q^+ is the phonon creation operator defined in Eq. (21), and m indexes the eigenstates of H with energies $\hbar\omega_m$. The absorption coefficient $\alpha(\omega)_j$ consists of a positive part $\sim |<m|\, a_q^+ |j>|^2$

which describes the photon-to-phonon process and a negative part $\sim|\langle m|a_q|j\rangle|^2$ which describes the phonon-to-photon process. At zero temperature, the physical absorption is correctly given by Eq. (44) if $|j\rangle$ is taken to be the ground state. In general, however, one should average $\alpha(w)_j$ over initial states. The actual absorption is proportional to

$$\alpha(\omega) = \sum_j P_j \alpha(\omega)_j , \tag{45}$$

where P_j is the probability of finding the system in the state $|j\rangle$. The following sum rule can be easily derived from the definition of $\alpha(\omega)$.

$$\int_0^\infty \alpha(\omega)\, d\omega = 1 \tag{46}$$

There are many aspects of nonlinear response to an applied field.[35] The only nonlinearity considered here is the effect of the applied field on the probabilities P_j. Physically, we are interested in how the absorption of the system changes as more and more phonons are created, and the P_j's are correspondingly altered.

In two special cases, the absorption coefficient can be easily calculated from Eqs. (44) and (45). The first case is the phonon limit, $\Gamma = 0$, where

$$\alpha(\omega) = \delta(\omega - \omega_q). \tag{47}$$

Here $\hbar\omega_q$ is the energy of a phonon with wavevector q. Since $\alpha(\omega)$ is independent of the P_j in this case, no saturation occurs and $\alpha(\omega)$ remains unchanged. The absorption line is infinitely sharp because no phonon decay or scattering processes are contained in the model Hamiltonian when $\Gamma = 0$.

The second simple example is the molecular limit where W = 0. Then

$$\alpha(\omega) = \sum_{m=0}^{\infty} (\tilde{P}_m - \tilde{P}_{m+1})\,(m+1)\,\delta(\omega - [\varepsilon - 2m\Gamma]/\hbar)\ . \qquad (48)$$

Here $\tilde{P}_m$ is the probability of finding any oscillator in its m^{th} excited state. If we assume that an oscillator is either in its ground state or its first excited state. Then $\tilde{P}_0 = 1 - C$ and $\tilde{P}_1 = C$, where C (Eq. (25)) is the density of excited oscillators, and $\alpha(\omega)$ becomes

$$\alpha(\omega) = 2C\,\delta(\omega - [\varepsilon - 2\Gamma]/\hbar) + (1-2C)\,\delta(\omega - \varepsilon/\hbar) \qquad (49)$$

In practice, C can be made non-zero by resonant excitation of a strong beam at $\hbar\omega \cong \varepsilon$. Then $\alpha(\omega)$ is the absorption spectrum observed by scanning a weak probe beam around $\hbar\omega \sim \varepsilon$ and $\hbar\omega \sim (\varepsilon - 2\Gamma)$. The peak at $\hbar\omega \cong \varepsilon$ decreases with increasing C as a result of saturation, while the peak at $\hbar\omega \cong \varepsilon - 2\Gamma$ describes absorption due to excitation of population in the first excited state to the next higher excited state. In the real spectrum, the δ function peaks would of course be broadened to peaks with finite widths.

When Γ and W are both nonzero, an exact calculation of $\alpha(\omega)$ is impossible. However, if Γ is not large compared with W, the mean-field approximation described in Section III may be justified. The absorption can be calculated after the interaction term in the Hamiltonian is factorized as was done in Eq. (24), the result is

$$\alpha(\omega) = \delta(\omega - (\omega_q - 4\,C\Gamma/\hbar))\ , \qquad (50)$$

and C is again the density of excited oscillators, or phonons per oscillator. There is no saturation, and the only nonlinear effect to be observed in the mean-field approximation corresponds to a line

shift to lower frequencies which occurs when a large number of phonons are created. For example, if $\Gamma = 50\ cm^{-1}$, a line shift of $2\ cm^{-1}$ would occur if one could create one phonon for every 100 oscillators.

One unrealistic feature of the mean-field approximation is that the interacting phonons appear to have infinite lifetimes. In fact, if W/Γ is not too small, Fermi's Golden Rule can give an estimate of the actual lifetime and the corresponding minimum linewidth, $\Delta\omega$,

$$\hbar(\Delta\omega) \gtrsim C\Gamma^2/W. \tag{51}$$

A second limitation of the mean field approximation is that it "breaks down" when W/Γ becomes small. This breakdown is signalled by the appearance of two-phonon bound states. An alternative approach is necessary to capture the effects of these bound states on the absorption coefficient. In the isolated molecule limit ($\Delta \to 0$), we know that the most important absorption peaks correspond to the transition from the lowest energy state to the first excited molecular vibrational state, and from the first to the second excited level. When Δ is small but nonzero we expect the two peaks to persist, but in this case an alternative description is that the first peak corresponds to the creation of an additional nearly-free phonon in the system and the second peak corresponds to the formation of a two-phonon bound state. The bound state is the combination of one phonon created by the photon and a second phonon which is already present in the system.

The absorption spectrum of N anharmonic oscillators with NC phonons cannot be easily calculated because the phonons interact through their anharmonicity. We circumvent this many-body problem by considering a smaller "reduced system" which initially has only one phonon in 1/C sites. This reduced system, which has the same phonon

density as the original system, exhibits two absorption peaks. The first peak at $\hbar\omega = \varepsilon_o$ results from one-photon excitation of a more or less free phonon at $q \cong 0$ where $\varepsilon_o = \varepsilon + \mathrm{sgn}(\Delta)W/2$ is the phonon energy. The second peak at $\hbar\omega = E_B - \varepsilon_o$ is due to one-photon excitation of the system from a one-phonon state to a two-phonon bound state with E_B as the binding energy. The probability that the system can be excited into a two-phonon bound state should be proportional to $|\langle\psi_F|\psi_B\rangle|^2$, as it is the square of the projection of the bound state on the two free phonon state. Following the definition of R in Eq. (38) and the approximation that the system initially has one phonon in N=1/C sites, we have

$$|\langle\psi_F|\psi_B\rangle|^2 = 2\,CR\,, \tag{52}$$

when C is small. The area under the secondary peak is thus 2CR, and from the sum rule (Eq. (46)) the area under the primary peak must be (1 - 2CR). Energy shifts and broadening of these peaks will be of order CW instead of $-4C\Gamma$ and $\sim C\Gamma^2/W$ as was the case for large W/Γ[18] (see Eqs. (50) and (51)). For the moment, we ignore the peak broadening and the small energy shifts to obtain a simple expression for the absorption in the semicircular model for $W/\Gamma \leqq 4$.

$$\alpha(\omega) = 2CR\,\delta(\omega - (\varepsilon_o - E_B)/\hbar) + (1 - 2CR)\,\delta(\omega - \varepsilon_o/\hbar) \tag{53}$$

Essentially the same absorption coefficient as is presented here was obtained in the molecular limit (Eq. (49)) except now the excited oscillator concentration C is scaled by R, and the absorption peak frequencies correspond to a q=0 phonon energy and the difference between the two-phonon bound state energy and a single q=0 phonon energy. The two expressions for the absorption (Eq. (53) and (49)) become identical as $W \to 0$. As in the molecular case, this $\alpha(\omega)$ is the

absorption spectrum seen by the weak probe beam, while C can be made nonzero by an intense pump beam at $\omega_0 \sim \varepsilon_0/\hbar$.

We are, of course, interested in seeing how the molecular character of the absorption disappears as W approaches 4Γ. The sign of Δ makes a big difference in this transition. When Δ is negative, indicating that q=0 phonons lie at the bottom of the band, increasing W/Γ moves the energy of two q=0 phonons and bound two-phonon states closer together and makes the latter look more like the former. This is reflected by the two absorption peaks in Eq. (53) approaching each other with the bound-state peak "stealing" intensity from the primary peak as they merge. For positive Δ, increasing W/Γ shifts the free and bound two-phonon states further apart. Consequently, the absorption peaks separate more and the bound-state peak gradually vanishes as $\frac{W}{\Gamma} \to 4$. The peak positions for both positive and negative Δ are shown as functions of W/Γ in Figure 4. Note the different frequency scales used for the two signs of Δ.

The absorption spectrum of Eq. (53) is unphysical because the peaks are infinitely narrow and the factor R diverges when Δ is negative. More sensible results are obtained if we assume the sharp peaks are actually Lorentzians with a half-width d. Physically, for negative Δ, R corresponds to the "size" of the two-phonon bound state, and this size appears to diverge as the binding energy goes to zero. In fact, R cannot exceed the average volume per phonon and still make sense. This can be seen formally in Eq. (53). Since $|\psi_F\rangle$ and $|\psi_B\rangle$ are normalized, 2CR should be less than one. The expressions for R in Eqs. (38) and (41) correspond to the large N or small C limits. The corresponding expressions for larger C are difficult to obtain. Here

we assume a simple interpolation formula for $|\langle\psi_F|\psi_B\rangle|^2$ which approaches the exact result for small C and satisfies the upper bound implied by Eq. (52).

$$|\langle\psi_F|\psi_B\rangle|^2 = 2C\,R/(1 + 2CR) \qquad (54)$$

This correction to $|\langle\psi_F|\psi_B\rangle|^2$ is at best only a reasonable guess. Actually, when 2CR becomes larger than one, the two-phonon bound state appreciably overlaps other single-phonon states and we are faced with truely unsoluble many-body effects. By using $|\langle\psi_F|\psi_B\rangle|^2$ as given by Eq. (54) we have artificially limited the two-particle bound state size so that the many-body effects appear to be small.

Practically speaking, the correction to R given in Eq. (54) is probably unimportant and unnecessary. Physically achievable phonon concentrations are usually small in macroscopic systems and it is unlikely that any many-body effects beyond the observation of two-phonon bound states will be detectable. However, a clear graphical presentation of the type of spectra one would expect from this model necessitates picking a relatively large C so that the secondary peak can be easily seen. The series of absorption spectra shown in Figure 5 are obtained from Eq. (53) using the approximate $|\langle\psi_F|\psi_B\rangle|^2$ (Eq. (54)) in place of 2CR, and the delta-function peaks are replaced by Lorentzians.

Spectra on the left in Figure 5 correspond to negative Δ and spectra on the right correspond to positive Δ. The spectra are shown for a sequence of values of $W/(4\Gamma) = 0$, 1/3, 2/3, and 1. The curves show the system passing from the molecular limit on top of the figure to the phonon limit at the bottom. Note that for graphical clarity, we needed different frequency scales for the different signs of Δ. We picked the phonon concentration C to be 0.03 for $\Delta < 0$ and C = 0.3 for

$\Delta > 0$. The peak half-widths, d, were chosen to be $0.1\,\Gamma$ for $\Delta < 0$ and $0.3\,\Gamma$ for $\Delta > 0$. The choices were again motivated by a desire to show pictorially how the secondary peak grows for positive Δ and shrinks for negative Δ. Note that for the case $\Delta < 0$ and $W/(4\Gamma)=2/3$, the secondary peak is actually larger than the primary peak even though the phonon concentration is only three percent.

VI. Discussion

Results presented here indicate that it is often not appropriate to view the phonon vs. local oscillator problem as a dicotomy. We showed in Section III that the phonon localization transition was gradual, and in subsequent sections we showed that systems which allow two-phonon bound states can exhibit spectral properties characteristic of both phonons and local oscillators.

We are hoping that the model presented here can be extended and applied to the point of giving difinitive comparisons with experiments. Some modifications will clearly be necessary to make these comparisons realistic. Many real materials (like HCl) are not characterized by one oscillator per unit cell. Dipole-dipole forces play an important role in the "interesting" modes of molecular crystals for which $W \tilde{\sim} \Gamma$ and one should modify the Δ's to incorporate the long range coupling. For other materials which might be described by $W \tilde{\sim} \Gamma$, like the transition metal carbides[15] and metal hydrides[16], one must consider all three phonon polarizations.

The stimulated Raman effect[37] is a good example of how theoretical results based on local oscillators can be very different from results obtained from a theory which uses phonons as basis states.[38] We feel

that careful applications of models similar to the one presented here could help resolve the sort of controversies which have appeared in the theory of the stimulated Raman effect.[38]

APPENDIX A

The full Hamiltonian obtained by quantizing the classical Hamiltonian is the phonon-conserving Hamiltonian H given in Eq. (4) plus additional terms given by

$$h = g \sum_n (a_n^+ + a_n)^3 + \sum_{n\neq m} \frac{\Delta_{nm}}{2} (a_n^+ a_m^+ + a_n a_m)$$
$$- \frac{\Gamma}{6} \sum_n \left\{ \begin{array}{l} a_n^+ a_n^+ a_n^+ a_n^+ + a_n a_n a_n a_n + \\ 4(a_n^+ a_n^+ a_n^+ a_n + a_n^+ a_n a_n a_n) \end{array} \right\} . \qquad \text{(A1)}$$

We seek a transformed Hamiltonian, H', given by

$$H' = e^{iS} [H + h] e^{-iS} , \qquad \text{(A2)}$$

with S chosen so that

$$i[S, H_o] = -h , \qquad \text{(A3)}$$

where

$$H_o = \varepsilon \sum_n a_n^+ a_n . \qquad \text{(A4)}$$

The required transformation is

$$S = - \frac{i}{2\varepsilon} \sum_{n\neq m} \Delta_{nm} (a_n^+ a_m^+ - a_n a_m) \qquad \text{(A5)}$$

$$- \frac{ig}{3\varepsilon} \sum_n \left\{ \begin{array}{l} a_n^+ a_n^+ a_n^+ - a_n a_n a_n + 9(a_n^+ a_n^+ a_n - a_n^+ a_n a_n) \\ \quad + 9(a_n^+ - a_n) \end{array} \right\}$$

$$- \frac{i\Gamma}{24\varepsilon} \sum_n \left\{ \begin{array}{l} a_n^+ a_n^+ a_n^+ a_n^+ - a_n a_n a_n a_n + 8(a_n^+ a_n^+ a_n^+ a_n - a_n^+ a_n a_n a_n) \\ + 12(a_n^+ a_n^+ - a_n a_n) \end{array} \right\} .$$

Note that S is small if ε is large compared to Δ, g, and Γ, so it makes sense to consider approximations to H which are low order in S. To first order in S, H' is identical to H given in Eq. (4). To second order,

$$H'_2 = H + i[S, (H - H_0 + \tfrac{1}{2}h)] \ , \tag{A6}$$

and H_2' also has phonon-conserving and phonon-nonconserving terms. The corrections to H are of order AB/ε where A and B are either a Δ, g or Γ. Again we argue that the phonon-nonconserving terms are relatively unimportant, and because they are smaller than before they will be ignored. If necessary these terms could be treated using perturbation theory or another unitary transformation. All except one of the phonon-conserving terms lead to a simple renormalization of the energies, ε, Δ_{nm}, and Γ which appears in the model Hamiltonian. The one additional phonon-conserving term which appears in H_2' is a three phonon interaction of the form

$$\frac{\Gamma^2}{\varepsilon} \sum_n a_n^+ a_n^+ a_n^+ a_n a_n a_n \ . \tag{A7}$$

We ignore this three particle interaction.

APPENDIX B

In order to obtain the bound state energy, E_B, and overlap probability, R, for the semicircular model, we first use Greens functions to obtain the corresponding quantities for the one-dimensional model. A simple alteration of the Greens function then yields the desired results for the semicircular model. We consider only the case in which the center-of-mass wavevector, q, is zero, and ignore this subscript. If the energy 2ε is also ignored, Eq. (35) becomes

$$H|m\rangle = 2\Delta\,(|m+1\rangle + |m-1\rangle) - 2\Gamma\,\delta_{m,o}|0\rangle\ . \tag{B1}$$

The Greens function is defined as

$$G(Z)_{nm} = \langle n|(Z-H)^{-1}|m\rangle, \tag{B2}$$

and the unperturbed Greens function ($G(Z)_{nm}{}^{o}$) is defined analogously except that Γ is taken to be zero. The free particle Greens function can be obtained by writing $|n\rangle$ as a linear combination of the plane wave eigenstates of the Hamiltonian for noninteracting particles, and for the one-dimensional model

$$G(Z)_{oo}{}^{o} = 1/\sqrt{Z^2 - (4\Delta)^2}\ . \tag{B3}$$

The perturbed Greens function can be written in terms of the free particle Greens function

$$G(Z)_{nm} = G(Z)_{nm}{}^{o} + G(Z)_{mo}{}^{o}\,2\Gamma\,G(Z)_{om}\ , \tag{B4}$$

from which it follows that

$$G(Z)_{nm} = G(Z)_{nm}{}^{o} + G(Z)_{no}{}^{o}\,[2\Gamma/(1+2\Gamma G(Z)_{oo}{}^{o})]G(Z)_{om}{}^{o}\ . \tag{B5}$$

The bound state is obtained from the isolated poles in G(z) which occur when

$$1 + 2\Gamma G(Z)_{oo}{}^{0} = 0\ . \tag{B6}$$

Except for the ignored constant, 2ε, solution of the above equation gives E_B of Eq. (36), when q = 0.

The corresponding bound state energy for the semicircular model is obtained by modifying the unperturbed Greens function. Since the density of states, $\rho(E)$, is related to the Green's function through

$$\rho(E) = \frac{1}{\pi} \lim_{\delta \to o^+} \left(\mathrm{Im}\, \{G(E+i\delta)_{oo}\}\right) , \tag{B7}$$

a Greens function of the form

$$G(Z)^S_{oo} = \frac{2}{W^2} \left(Z - \sqrt{Z^2 - W^2}\right) \tag{B8}$$

has the correct analytic structure, and yields the desired density of states (of width 2W because 2 phonons are involved). A solution of $1+2\Gamma\, G(E_B)^S_{oo} = 0$ gives

$$E_B = -\frac{W}{2}\left(\frac{4\Gamma}{W} + \frac{W}{4\Gamma}\right) \qquad \text{for } \Gamma > W/4 , \tag{B9}$$

which is essentially the result of Eq. (41). The apparent solution for smaller Γ corresponds to taking the wrong sign of the square root in Eq. (B8).

The normalized probabilities $R = \frac{1}{2} N |\langle \psi_F | \psi_B \rangle|^2$ can also be obtained from Greens functions. To do this, let

$$g(z) = \langle \psi_F | \frac{1}{Z-H} | \psi_F \rangle . \tag{B10}$$

One of the eigenstates of H is $|\psi_B\rangle$, so an expansion of g(z) in terms of the eigenstates of H gives

$$g(z) = |\langle \psi_F | \psi_B \rangle|^2 \frac{1}{Z-E_B} + (\text{terms nonsingular as } z \to E_B) . \tag{B11}$$

Let η be a number much smaller than the difference between E_B and all other eigenvalues of H. Then

$$\lim_{\delta \to o} \int_{E_B - \eta}^{E_B + \eta} g(E+i\delta)\, dE = -i\pi |\langle \psi_B | \psi_F \rangle|^2 + (\text{terms which vanish with } \eta) \tag{B12}$$

We can take the limit of small k_1 and k_2 in $|\psi_F\rangle$, and in this limit

$$g(z) = \frac{2}{N} \sum_{nm} G(z)_{nm} . \tag{B13}$$

Writing $G(z)_{nm}$ in terms of $G(z)^o_{nm}$ (Eq. (B5)),

$$g(z) = \frac{2}{z-2\varepsilon_o} + \frac{2}{N} \frac{1}{(z-2\varepsilon_o)^2} \frac{2\Gamma}{1+2\Gamma G(z)^o_{oo}} \quad . \tag{B14}$$

We know that $1 + 2\Gamma G(E_B)^o_{oo} = 0$, so for z near E_B,

$$1 + 2\Gamma G(z)^o_{oo} \approx (z-E_B) \frac{d}{dz} (G(z)^o_{oo}) \Big| z = E_B \quad . \tag{B15}$$

In the limit of small η, only the singular part of g(z) contributes to the integral of Eq. (B12), and using Eq. (B15),

$$\frac{2}{N} \frac{1}{(E_B-2\varepsilon_o)^2 \frac{d}{dz} (G(z)^o_{oo})\Big|_{z=E_B}} = |\langle\psi_F|\psi_B\rangle|^2 \quad ,$$

or

$$R = [(E_B-2\varepsilon_o)^2 \frac{d}{dz} (G(z)^o_{oo})\Big|_{z=E_B}]^{-1} \quad . \tag{B16}$$

When the values of E_B, $\varepsilon_o = W/2$ sign Δ, and $G(z)^o_{oo}$ appropriate for the one-dimensional model are substituted into the above expression for R, Eq. (39) is obtained. When $G(z)^o_{oo}$ is replaced by $G(z)^s_{oo}$ and E_B is given by (B9), the value of R for the semicircular model, Eq. (42), is obtained.

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FIGURE CAPTIONS

Figure 1 The phase diagram for the model Hamiltonian showing the temperature ranges where local oscillators and extended phonons minimize the free energy as functions of the normalized phonon dispersion $\bar{W}/\Gamma$. In practice, the transition between the two regions will be continuous and no phase transition is expected.

Figure 2 Energy levels of the doubly excited model Hamiltonian with a semicircular density of states (the semicircular model) as functios of W/Γ. The bound states disappear for W/Γ greater than four.

Figure 3 The normalized probabilities, R, of optically creating two-phonon bound states, for the semicircular model, as functions of W/Γ. The upper curve corresponds to negative Γ and the lower curve corresponds to positive Γ. Note the logarithmic scale.

Figure 4 The frequencies of the primary (photon → free phonon) and secondary (photon + phonon → two-phonon bound state) peaks in the absorption spectrum of the semicircular model as functions of W/Γ. The upper line describes the primary peak and the lower curve describes the secondary peak in both cases. Note that the frequency scale on the left corresponding to $\Delta < 0$ differs from the scale on the

right where $\Delta > 0$. The secondary peak disappears with the bound state for $W = 4\Gamma$.

Figure 5 The transition in the absorption spectrum, $\alpha(\omega)$, from that characterizing local oscillators (top) to that characterizing phonons (bottom) for the semicircular model. The series of spectra correspond to (from top to bottom) $W/(4\Gamma) = 0, 1/3, 2/3, 1$. Note the different frequency scales for the spectra on the left ($\Delta < 0$) and those on the right ($\Delta > 0$).

The secondary peak (if visible) lies at a lower frequency than the primary peak in each case. The arrow on the lower right spectrum indicates the position of the secondary peak as its intensity vanishes. Peaks in $\alpha(\omega)$ were given a Lorentzian shape and a half-width $d = 0.1\,\Gamma$ for $\Gamma < 0$ and $d = 0.3\,\Gamma$ for $\Delta > 0$. The phonon concentration C was taken to be 0.03 for $\Delta < 0$ and 0.3 for $\Delta > 0$. The somewhat unreasonable parameters were chosen purely for the purpose of illustrating the spectral transition.

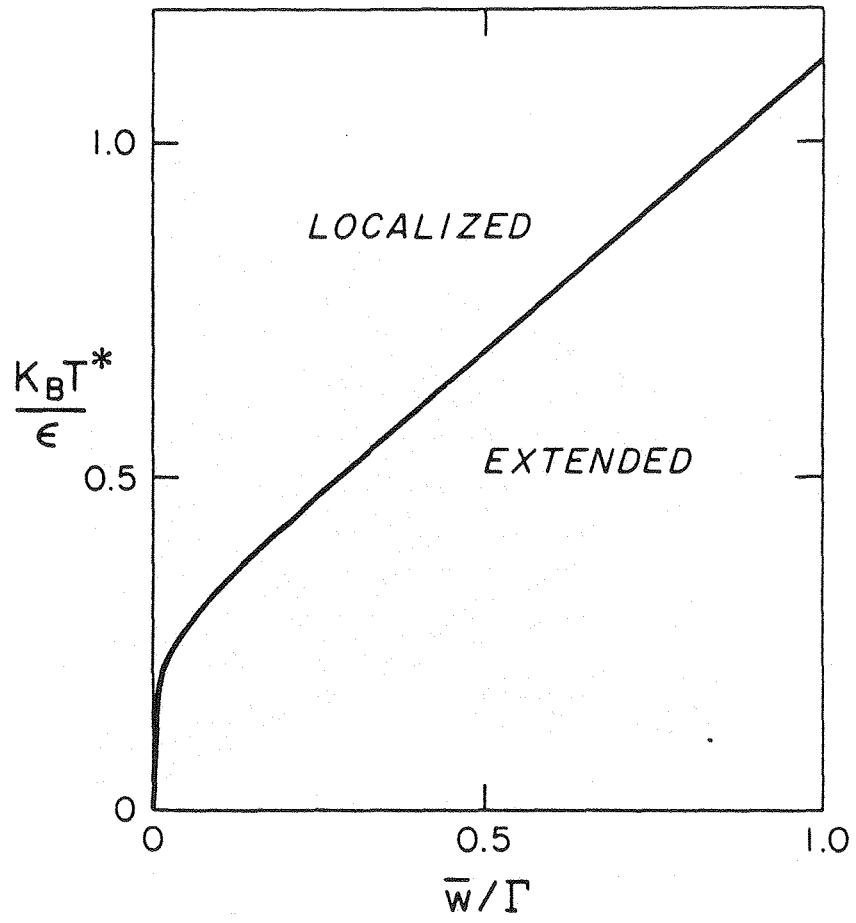

1.0
LOCALIZED
$\frac{K_B T^*}{\epsilon}$
EXTENDED
0.5
0
0
0.5
1.0
$\bar{w}/\Gamma$

Figure 1

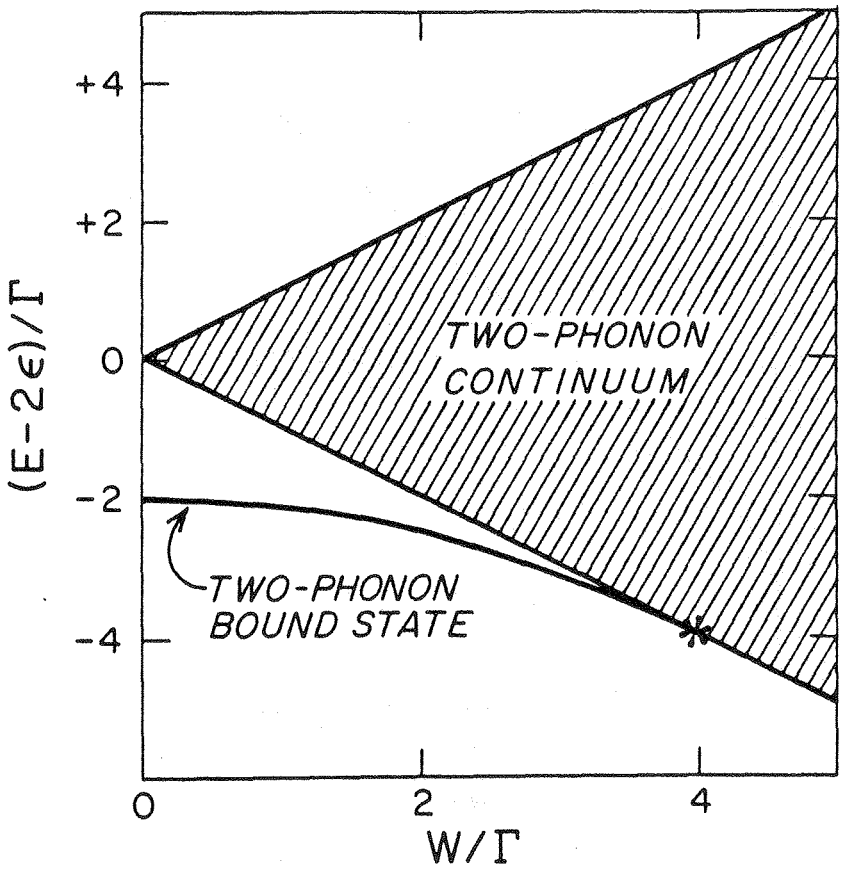

+4
+2
0
-2
-4
(E-2ε)/Γ
TWO-PHONON
CONTINUUM
TWO-PHONON
BOUND STATE
0
2
4
W/Γ

Figure 2

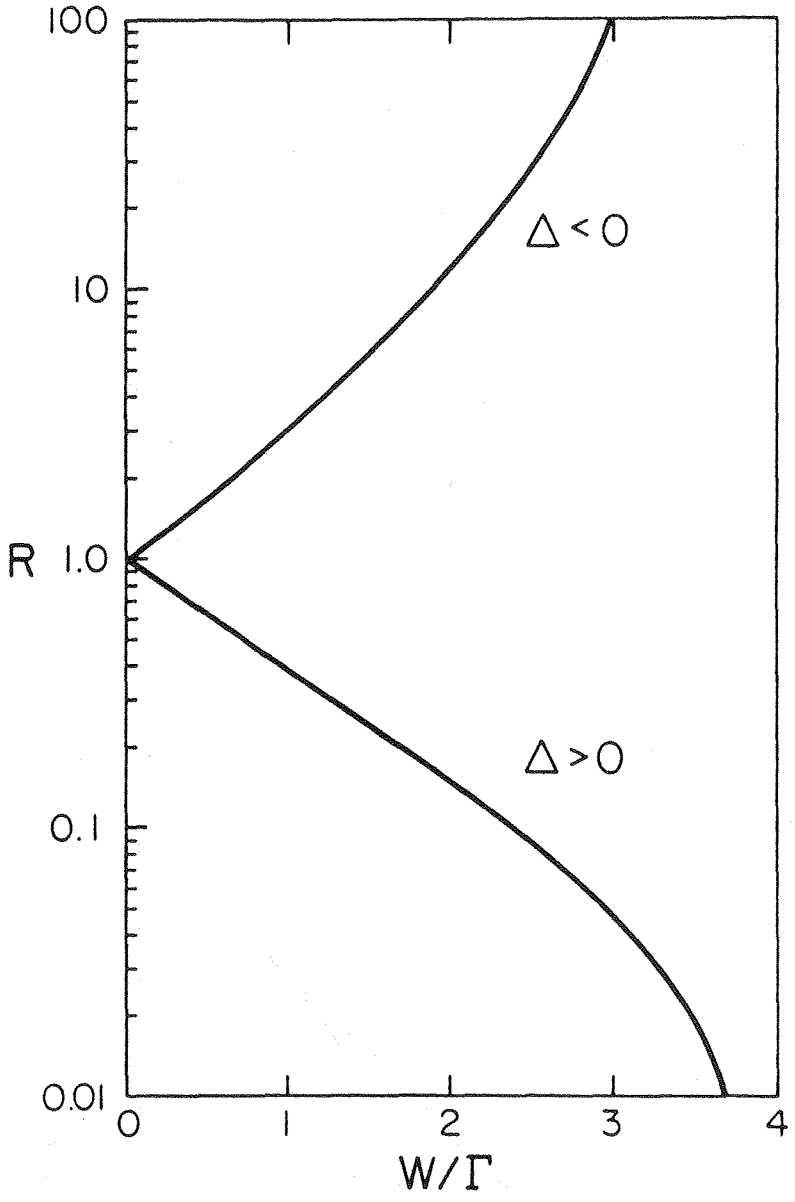
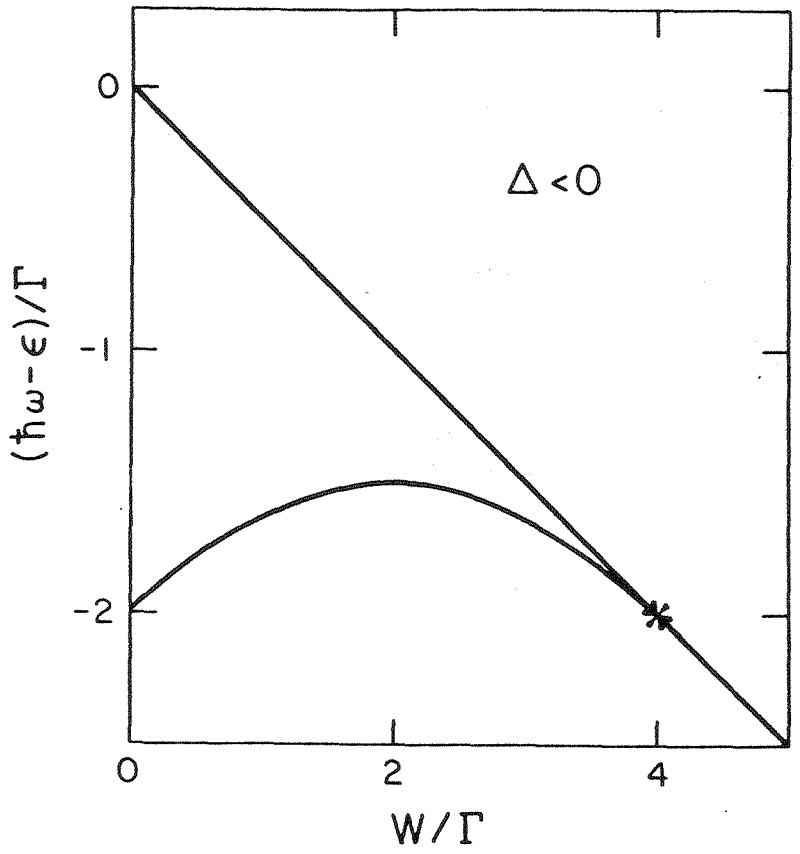


Figure 3



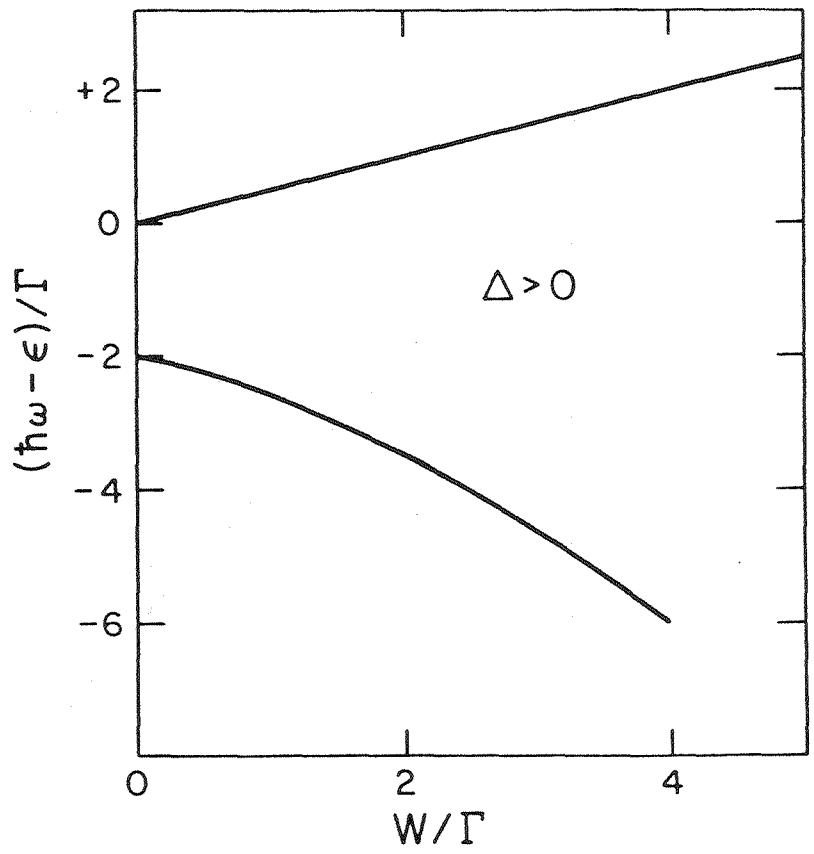


Figure 4

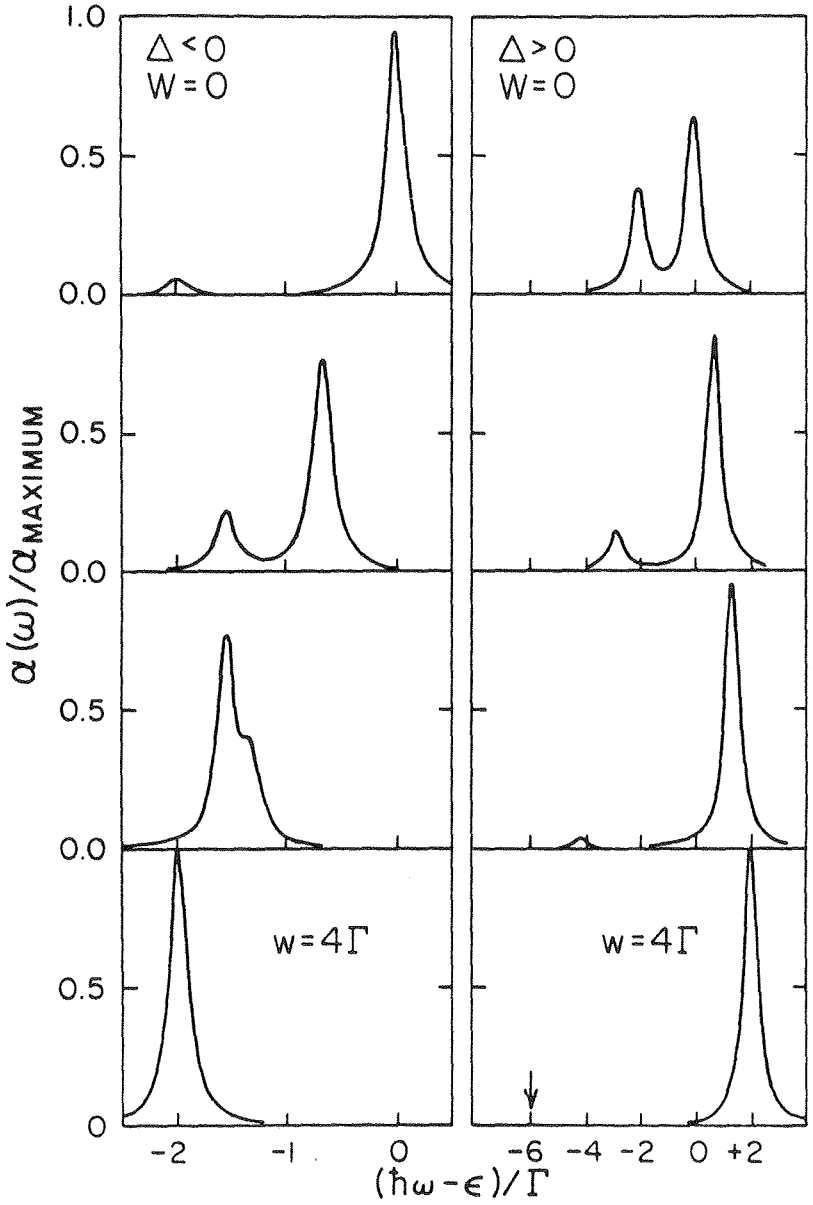

1.0
0.5
0.0
0.5
0.0
0.5
0.0
0.5
0
Δ<0
W=0
Δ>0
W=0
w=4Γ
w=4Γ
α(ω)/α MAXIMUM
-2
-1
0
-6
-4
-2
0
+2
(ħω-ε)/Γ

Figure 5